Quantum-Classical Dynamics of Wave Fields

Alessandro Sergi *
Dipartimento di Fisica, Universitá degli Studi di Messina, Contrada Papardo 98166 Messina, Italy

An approach to the quantum-classical mechanics of phase space dependent operators, which has been proposed recently, is remodeled as a formalism for wave fields. Such wave fields obey to a system of coupled non-linear equations that can be written by means of a suitable non-Hamiltonian bracket. As an example, the theory is applied to the relaxation dynamics of the spin-boson model. In the adiabatic limit, a good agreement with calculations performed by the operator approach is obtained. Moreover, the theory proposed in this paper can take nonadiabatic effects into account without resorting to surface-hopping approximations. Hence, the results obtained follow qualitatively those of previous surface-hopping calculations and increase by a factor of (at least) two the time length over which nonadiabatic dynamics can be propagated with small statistical errors. Moreover, it is worth to note that the dynamics of quantum-classical wave fields here proposed is a straightforward non-Hamiltonian generalization of the formalism for non-linear quantum mechanics that Weinberg introduced recently.

I. INTRODUCTION

There are many instances where a quantum-classical description is a useful approximation to full quantum dynamics. Typically, a quantum-classical picture often allows one to implement calculable algorithms on computer, for example, whenever charge transfer is considered within complex environments, such as those provided by proteins or nano-systems in general [1]. With respect to this, an algebraic approach has been recently proposed [2, 3] in order to formulate the dynamics and the statistical mechanics [4] of quantum-classical systems. Such an approach represents quantum-classical dynamics by means of suitable brackets of phase space dependent operators and describes consistently the back-reaction between quantum and classical degrees of freedom. Notably, a particular implementation of this formalism has been used to calculate nonadiabatic rate constants in systems modeling chemical reactions in the condensed phase [5]. However, such schemes have only permitted the simulation of short-time nonadiabatic dynamics because of the time-growing statistical error of the algorithm. Nevertheless, the algebraic approach [2, 3], underlying the algorithms of Refs. [5], has some very nice features, such as the (above mentioned) proper description of the back-reaction between degrees of freedom, that one should not give up when addressing quantum-classical statistical mechanics. Moreover, quantum-classical brackets define a non-Hamiltonian algebra [6] so that their matrix structure allows one to introduce quantum-classical Nosé-Hoover dynamics [6] and to define the statistical mechanics of quantum-classical systems with holonomic constraints [7]. All the above features of the formalism are highly desirable when studying complex systems in the condensed phase. Therefore, it is worth to search for a reformulation of the theory of Refs. [5–7] that, while maintaining such features, could be used to integrate reliably long-time nonadiabatic dynamics.

For this sake, one can note that, within standard quantum mechanics, some problems that are formidable to solve by means of the dynamics of operators become much simpler to handle when, instead, the time evolution of wave functions is considered [8]. Hence, for analogy, it might also happen that, within quantum-classical mechanics, the correspondence between operators and quantum-classical wave functions could open new possibilities for useful approximations in order to carry long-time calculations efficiently. Indeed, finding and applying the correspondence between operator and wave scheme of motion in quantum-classical mechanics is the scope of the present paper. A wave picture for quantum-classical dynamics can be found by direct algebraic manipulation of the equation of motion for the density matrix. In practice, the single equation obeyed by the quantum-classical density matrix is mapped onto two coupled non-linear equations for quantum-classical wave fields. Despite its non-linear character, such a quantum-classical dynamics of phase space dependent wave fields corresponds exactly to the dynamics of phase space dependent operators discussed in Refs. [2, 3, 5–7] and can be used to devise novel algorithms and approximation schemes.

The abstract algebraic equations here presented are readily expressed in the adiabatic basis and applied, in order to provide an illustrative example, to the spin-boson model and its relaxation dynamics both in the adiabatic and nonadiabatic limit. By making a suitable equilibrium approximation to the non-linear wave equations, it is found that nonadiabatic dynamics can be propagated, within the wave picture, for time intervals that are a factor of two-three longer than those which have been spanned in Refs. [9] by means of the operator theory [2, 3, 5–7]. Such a result is very encouraging for pursuing the long-time integration of the nonadiabatic dynamics of complex systems in the condensed phase.

Following a line of research that investigates the relations between classical and quantum theories [10]. it is worth to note that the wave schemes of motion in

*E-mail: asergi@unime.it

quantum-classical mechanics, which is introduced in this paper, generalizes within a non-Hamiltonian framework the elegant formalism that Weinberg [11] proposed for describing eventual non-linear effects in quantum mechanics [12],

This paper is organized as follows. In Section II the non-Hamiltonian algebra of phase space dependent operators is briefly summarized. In Section III the quantum-classical dynamics of operators, is transformed into a theory for phase space dependent wave fields evolving in time. Such a theory for wave fields is also expressed by means of suitable non-Hamiltonian brackets: in this way a link is found with the generalization of Weinberg's non-linear formalism given in Appendix A. More specifically, in Appendix A, Weinberg's formalism is briefly reviewed and its symplectic structure is unveiled. Then, this structure is generalized by means of non-Hamiltonian brackets. Therefore, one can appreciate how the generalized Weinberg's formalism establishes a more comprehensive mathematical framework for non-linear equations of motion which comprises phase space dependent wave fields as a special case. In Section IV the abstract non-linear equations of motion for quantum classical fields are represented in the adiabatic basis and some considerations, which are pertinent to numerical implementations, are made. By making an equilibrium *ansatz*, in Section V the non-linear equations of motion are put into a linear form and the theory is applied to the spin-boson model. Section VI is devoted to conclusions and perspectives.

II. NON-HAMILTONIAN MECHANICS OF QUANTUM-CLASSICAL OPERATORS

A quantum-classical system is composed of both quantum $\hat{\chi}$ and classical X degrees of freedom, where $X = (R, P)$ is the phase space point, with R and P coordinates and momenta, respectively. Within the operator formalism of Refs. [2, 3, 6, 7], the quantum variables depends from the classical point X of phase space. The energy of the system is defined in terms of a Hamiltonian operator $\hat{H} = \hat{H}(X)$ which couples quantum and classical variables, by $E = \mathrm{Tr}' \int dX \hat{H}(X)$. The dynamical evolution of a quantum-classical operator $\hat{\chi}(X)$ is given by [2, 3]

$$\begin{aligned} \frac{d}{dt}\hat{\chi}(X,t) &= \frac{i}{\hbar}\left[\hat{H},\hat{\chi}(X,t)\right]_{\boldsymbol{\mathcal{B}}} - \frac{1}{2}\left\{\hat{H},\hat{\chi}(X,t)\right\}_{\boldsymbol{\mathcal{B}}} \\ &+ \frac{1}{2}\left\{\hat{\chi}(X,t),\hat{H}\right\}_{\boldsymbol{\mathcal{B}}} = \left(\hat{H},\hat{\chi}(X,t)\right) , \quad (1) \end{aligned}$$

where

$$\left[\hat{H},\hat{\chi}\right]_{\boldsymbol{\mathcal{B}}} = \left[\begin{array}{cc}\hat{H} & \hat{\chi}\end{array}\right]\cdot\boldsymbol{\mathcal{B}}\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\chi}\end{array}\right] \quad (2)$$

is the commutator and

$$\{\hat{H},\hat{\chi}\}_{\boldsymbol{\mathcal{B}}} = \sum_{i,j=1}^{2N}\frac{\partial\hat{H}}{\partial X_i}\mathcal{B}_{ij}\frac{\partial\hat{\chi}}{\partial X_j} \quad (3)$$

is the Poisson bracket [13]. Both the commutator and the Poisson bracket are defined in terms of the antisymmetric matrix

$$\boldsymbol{\mathcal{B}} = \left[\begin{array}{cc}0 & 1\\ -1 & 0\end{array}\right] . \quad (4)$$

The last equality in Eq. (1) defines the quantum-classical bracket. Following Refs. [6, 7, 14], the quantum-classical law of motion can be easily casted in matrix form as

$$\begin{aligned} \frac{d}{dt}\hat{\chi} &= \frac{i}{\hbar}\left[\begin{array}{cc}\hat{H} & \hat{\chi}\end{array}\right]\cdot\boldsymbol{\mathcal{D}}\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\chi}\end{array}\right] \\ &= \frac{i}{\hbar}[\hat{H},\hat{\chi}]_{\boldsymbol{\mathcal{D}}} , \quad (5) \end{aligned}$$

where

$$\boldsymbol{\mathcal{D}} = \left[\begin{array}{cc}0 & 1-\frac{\hbar}{2i}\{\ldots,\ldots\}_{\boldsymbol{\mathcal{B}}}\\ -1+\frac{\hbar}{2i}\{\ldots,\ldots\}_{\boldsymbol{\mathcal{B}}} & 0\end{array}\right] . \quad (6)$$

The structure of Eq. (5) is that of a non-Hamiltonian commutator, which will be defined below in Eq. (10), and as such generalizes the standard quantum law of motion [6]. The antisymmetric super-operator $\boldsymbol{\mathcal{D}}$ in Eq. (6) introduces a novel mathematical structure that characterizes the time evolution of quantum-classical systems. The Jacobi relation in quantum-classical dynamics is

$$\mathcal{J} = \left[\hat{\chi},\left[\hat{\xi},\hat{\eta}\right]_{\boldsymbol{\mathcal{D}}}\right]_{\boldsymbol{\mathcal{D}}} + \left[\hat{\eta},\left[\hat{\chi},\hat{\xi}\right]_{\boldsymbol{\mathcal{D}}}\right]_{\boldsymbol{\mathcal{D}}} + \left[\hat{\xi},[\hat{\eta},\hat{\chi}]_{\boldsymbol{\mathcal{D}}}\right]_{\boldsymbol{\mathcal{D}}} . \quad (7)$$

The explicit expression of $\mathcal{J}$ has been given in Ref. [6] where it was shown that it may be different from zero at least in some point X of phase space: for this reason the quantum-classical theory of Refs [2, 3, 6, 7] can be classified as a non-Hamiltonian theory.

It is worth to note that the quantum-classical law of motion in Eq. (5) is a particular example of a more general form of quantum mechanics where time evolution is defined by means of non-Hamiltonian commutators. The non-Hamiltonian commutator between two arbitrary operators $\hat{\chi}$ and $\hat{\xi}$ is defined by

$$[\hat{\chi},\hat{\xi}]_{\boldsymbol{\Omega}} = \left[\begin{array}{cc}\hat{\chi} & \hat{\xi}\end{array}\right]\cdot\boldsymbol{\Omega}\cdot\left[\begin{array}{c}\hat{\chi}\\ \hat{\xi}\end{array}\right] , \quad (8)$$

where $\boldsymbol{\Omega}$ is an antisymmetric matrix operator of the form

$$\boldsymbol{\Omega} = \left[\begin{array}{cc}0 & f[\hat{\eta}]\\ -f[\hat{\eta}] & 0\end{array}\right] , \quad (9)$$

where $f[\hat{\eta}]$ can be another arbitrary operator or functional of operators. Then, generalized equations of motion can be defined as

$$\begin{aligned} \frac{d\hat{\chi}}{dt} &= \frac{i}{\hbar}\left[\begin{array}{cc}\hat{H} & \hat{\chi}\end{array}\right]\cdot\boldsymbol{\Omega}\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\chi}\end{array}\right] \\ &= \frac{i}{\hbar}[\hat{H},\hat{\chi}]_{\boldsymbol{\Omega}} . \quad (10) \end{aligned}$$

The non-Hamiltonian commutator of Eq. (8) defines a generalized form of quantum mechanics where, nevertheless, the Hamiltonian operator $\hat{H}$ is still a constant of motion because of the antisymmetry of $\boldsymbol{\Omega}$.

III. QUANTUM-CLASSICAL WAVE DYNAMICS

In Refs. [2, 3], quantum-classical evolution has been formulated in terms of phase space dependent operators. In this scheme of motion operators evolve according to

$$\begin{aligned}\hat{\chi}(X,t) &= \exp\left\{t\left[\hat{H},\ldots\right]_{\boldsymbol{\mathcal{D}}}\right\}\hat{\chi}(X)\\ &= \exp\left\{it\mathcal{L}\right\}\hat{\chi}(X)\,,\end{aligned} \tag{11}$$

where the last equality defines the quantum-classical Liouville propagator. Quantum-classical averages are calculated as

$$\begin{aligned}\langle\hat{\chi}\rangle(t) &= \mathrm{Tr}'\int dX\hat{\rho}(X)\hat{\chi}(X,t)\\ &= \mathrm{Tr}'\int dX\hat{\rho}(X,t)\hat{\chi}(X)\,,\end{aligned} \tag{12}$$

where $\hat{\rho}(X)$ is the quantum-classical density matrix and $\hat{\rho}(X,t) = \exp\{-it\mathcal{L}\}\,\hat{\rho}(X)$. Either evolving the dynamical variables or the density matrix, one is still dealing with phase space dependent operators: *viz.*, one deals with a form of generalized quantum-classical matrix mechanics. As it has been discussed in the Introduction, this theory has interesting formal features and a certain number of numerical schemes have been proposed to integrate the dynamics and calculate correlation functions [5, 9, 15]. However, these algorithms have been applied with success only to short-time dynamics because of statistical uncertainties that grows with time beyond numerical tolerance. With this in mind, it is interesting to see which features are found when the quantum-classical theory of Refs. [2, 3] is mapped into a scheme of motion where phase space dependent wave fields, instead of operators, are used to represent the dynamics.

As it is well known [8], in standard quantum mechanics, the correspondence between dynamics in the Heisenberg and in the Schrödinger picture rests ultimately on the following operator identity:

$$e^{\hat{Y}}\hat{X}e^{-\hat{Y}} = e^{[\hat{Y},\ldots]}\hat{X}\,, \tag{13}$$

where $[\hat{Y},\ldots]\hat{X} \equiv [\hat{Y},\hat{X}]$. Thus, in quantum-classical theory, one would like to derive an operator identity analogous to that in Eq. (13). However, as already shown in Ref. [4], because of the non associativity of the quantum-classical bracket in Eq. (5), the identity that can be derived is

$$e^{\frac{it}{\hbar}\,[\hat{H},\ldots]_{\boldsymbol{\mathcal{D}}}}\hat{\chi} = \mathcal{S}\left(e^{\frac{it}{\hbar}\overrightarrow{\mathcal{H}}}\hat{\chi}e^{-\frac{it}{\hbar}\overleftarrow{\mathcal{H}}}\right)\,, \tag{14}$$

where the two operators

$$\overrightarrow{\mathcal{H}} = \hat{H} - \frac{\hbar}{2i}\left\{\hat{H},\ldots\right\}_{\boldsymbol{\mathcal{B}}} \tag{15}$$

$$\overleftarrow{\mathcal{H}} = \hat{H} - \frac{\hbar}{2i}\left\{\ldots,\hat{H}\right\}_{\boldsymbol{\mathcal{B}}} \tag{16}$$

have been introduced and $\mathcal{S}$ is an ordering operator which is chosen so that the left and the right hand side of Eq. (14), when the exponential operators are substituted with their series expansion, coincide by construction [4]. The existence of such an ordering problem, and of the ordering operator $\mathcal{S}$, in Eq. (14) is caused by the Poisson bracket parts of the operators in Eqs. (15) and (16). Hence, one can imagine that the solution of this problem can be found by dealing properly with this part of the bracket. Indeed, this can be achieved. To this end, one can consider the quantum-classical equation of motion for the density matrix

$$\begin{aligned}\frac{\partial\hat{\rho}}{\partial t} &= -\frac{i}{\hbar}\left[\,\hat{H}\;\;\hat{\rho}\,\right]\\ &\cdot\left[\begin{array}{cc}0 & 1-\frac{\hbar}{2i}\{\ldots,\ldots\}_{\boldsymbol{\mathcal{B}}}\\ -1+\frac{\hbar}{2i}\{\ldots,\ldots\}_{\boldsymbol{\mathcal{B}}} & 0\end{array}\right]\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\rho}\end{array}\right]\,.\end{aligned} \tag{17}$$

As above discussed, in Eq. (17) the ordering problem arises from the terms in the right hand side containing the Poisson bracket operator $\{\ldots,\ldots\}_{\boldsymbol{\mathcal{B}}}$. Then, considering the identity $1 = \hat{\rho}\cdot\hat{\rho}^{-1} = \hat{\rho}^{-1}\cdot\hat{\rho}$, Eq. (17) can be rewritten as

$$\begin{aligned}\partial_t\hat{\rho} &= -\frac{i}{\hbar}\left[\,\hat{H}\;\;\hat{1}\,\right]\\ &\cdot\left[\begin{array}{cc}0 & 1-\frac{\hbar}{2i}\{\ldots,\hat{\rho}\}_{\boldsymbol{\mathcal{B}}}\\ -1+\frac{\hbar}{2i}\{\hat{\rho},\ldots\}_{\boldsymbol{\mathcal{B}}} & 0\end{array}\right]\cdot\left[\begin{array}{c}\hat{H}\\ \hat{1}\end{array}\right]\\ &= -\frac{i}{\hbar}\left[\,\hat{H}\;\;\hat{\rho}\hat{\rho}^{-1}\,\right]\\ &\cdot\left[\begin{array}{cc}0 & 1-\frac{\hbar}{2i}\{\ldots,\hat{\rho}\}_{\boldsymbol{\mathcal{B}}}\\ -1+\frac{\hbar}{2i}\{\hat{\rho},\ldots\}_{\boldsymbol{\mathcal{B}}} & 0\end{array}\right]\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\rho}^{-1}\hat{\rho}\end{array}\right]\\ &= -\frac{i}{\hbar}\left[\,\hat{H}\;\;\hat{\rho}\,\right]\cdot\boldsymbol{\mathcal{D}}_{\boldsymbol{\mathcal{B}},[\hat{\rho}]}\cdot\left[\begin{array}{c}\hat{H}\\ \hat{\rho}\end{array}\right]\,,\end{aligned} \tag{18}$$

where

$$\boldsymbol{\mathcal{D}}_{\boldsymbol{\mathcal{B}},[\hat{\rho}]} = \left[\begin{array}{cc}0 & 1-\frac{\hbar}{2i}\{\ldots,\ln(\hat{\rho})\}_{\boldsymbol{\mathcal{B}}}\\ -1+\frac{\hbar}{2i}\{\ln(\hat{\rho}),\ldots\}_{\boldsymbol{\mathcal{B}}} & 0\end{array}\right] \tag{19}$$

The operator $\boldsymbol{\mathcal{D}}_{\boldsymbol{\mathcal{B}},[\hat{\rho}]}$ in Eq. (19) depends from the quantum-classical density matrix, $\hat{\rho}$, itself. However, if one momentarily disregards this non-linear dependence, Eq. (18) can be manipulated algebraically in order to develop a wave picture of quantum-classical mechanics. To this end, one can introduce quantum-classical wave fields, $|\psi(X)\rangle$ and $\langle\psi(X)|$, and make the following *ansatz* for the density matrix

$$\hat{\rho}(X) = \sum_{\iota} w_\iota|\psi^\iota(X)\rangle\langle\psi^\iota(X)|\,, \tag{20}$$

where one has assumed that, because of thermal disorder, there can be many microscopic states $|\psi^\iota(X)\rangle$ ($\iota = 1,\ldots,l$) which correspond to the same value of the

macroscopic relevant observables [16]. In terms of the quantum-classical wave fields $|\psi^\iota(X)\rangle$ and $\langle\psi^\iota(X)|$, and considering the single state labeled by ι, Eq. (18) becomes

$$\begin{aligned} |\dot{\psi}^\iota(X)\rangle\langle\psi^\iota(X)| &+ |\psi^\iota(X)\rangle\langle\dot{\psi}^\iota(X)| = \\ &- \frac{i}{\hbar}\Big(\hat{H}|\psi^\iota(X)\rangle\langle\psi^\iota(X)| \\ &+ |\psi^\iota(X)\rangle\langle\psi^\iota(X)|\hat{H}\Big) \\ &+ \frac{1}{2}\Big(\Big\{\hat{H},\ln(\hat{\rho})\Big\}_{\mathcal{B}}|\psi^\iota(X)\rangle\langle\psi^\iota(X)| \\ &- |\psi^\iota(X)\rangle\langle\psi^\iota(X)|\Big\{\ln(\hat{\rho}),\hat{H}\Big\}_{\mathcal{B}}\Big) \ . \end{aligned} \tag{21}$$

Equation (21) can be written as a system of two coupled equations for the wave fields [17]:

$$\begin{aligned} i\hbar\frac{d}{dt}|\psi^\iota_{(X,t)}\rangle &= \left(\hat{H} - \frac{\hbar}{2i}\Big\{\hat{H},\ln(\hat{\rho}_{(X,t)})\Big\}_{\mathcal{B}}\right)|\psi^\iota_{(X,t)}\rangle \\ -i\hbar\langle\psi^\iota_{(X,t)}|\frac{\overleftarrow{d}}{dt} &= \langle\psi^\iota_{(X,t)}|\left(\hat{H} - \frac{\hbar}{2i}\Big\{\ln(\hat{\rho}_{(X,t)}),\hat{H}\Big\}_{\mathcal{B}}\right) \ . \end{aligned} \tag{22}$$

Equations (22), obeyd by the wave fields, are non-linear since their solution depend self-consistently from the density matrix defined in Eq. (20). These equations are also non-Hermitian since the operators $\Big\{\hat{H},\ln(\hat{\rho})\Big\}_{\mathcal{B}}$ and $\Big\{\ln(\hat{\rho}),\hat{H}\Big\}_{\mathcal{B}}$ are not Hermitian. However, this does not cause problems for the conservation of probability. The wave fields $|\psi^\iota\rangle$ and $\langle\psi^\iota|$ evolve according to the different propagators

$$\overrightarrow{\mathcal{U}}_{\mathcal{B},[\hat{\rho}]}(t) = \exp\left[-\frac{it}{\hbar}\left(\hat{H} - \frac{\hbar}{2i}\Big\{\hat{H},\ln(\hat{\rho})\Big\}_{\mathcal{B}}\right)\right] \ , \tag{23}$$

$$\overleftarrow{\mathcal{U}}_{\mathcal{B},[\hat{\rho}]}(t) = \exp\left[-\frac{it}{\hbar}\left(\hat{H} - \frac{\hbar}{2i}\Big\{\ln(\hat{\rho}),\hat{H}\Big\}_{\mathcal{B}}\right)\right] \ , \tag{24}$$

so that time-propagating wave fields are defined by

$$|\psi^\iota(X,t)\rangle = \overrightarrow{\mathcal{U}}_{\mathcal{B},[\hat{\rho}]}(t)|\psi^\iota(X)\rangle \tag{25}$$

$$\langle\psi^\iota(X,t)| = \langle\psi^\iota(X,)|\overleftarrow{\mathcal{U}}_{\mathcal{B},[\hat{\rho}]}(t) \ . \tag{26}$$

Quantum classical averages can be written as

$$\langle\hat{\chi}\rangle(t) = \int dX\sum_\iota w_\iota\langle\psi^\iota(X,t)|\hat{\chi}|\psi^\iota(X,t)\rangle \ . \tag{27}$$

One can always transform back to the operator picture to show that probability is conserved.

A. Non-linear wave dynamics by means of non-Hamiltonian brackets

The wave equations in (22) were derived starting from the non-Hamiltonian commutator expressing the dynamics of phase space dependent operators [6]. It is interesting to recast quantum-classical wave dynamics itself by means of non-Hamiltonian brackets. It turns out that this form of the wave equations generalizes the mathematical formalism first proposed by Weinberg [11] in order to study possible non-linear effects in quantum mechanics (see Appendix A).

Consider a case in which a single state is present, *i.e.* $\iota = 1$. Then, consider the wave fields $|\psi\rangle$ and $\langle\psi|$ as coordinates of an abstract space, and denote the point of such a space as

$$\boldsymbol{\zeta} = \begin{bmatrix} |\psi\rangle \\ \langle\psi| \end{bmatrix} \ . \tag{28}$$

Introduce the function

$$\mathcal{H} = \langle\psi|\hat{H}|\psi\rangle \ , \tag{29}$$

and the antisymmetric matrix operator

$$\boldsymbol{\Omega} = \begin{bmatrix} 0 & 1 - \frac{\hbar}{2i}\frac{\left\{\hat{H},\ln(\hat{\rho})\right\}_{\mathcal{B}}|\psi\rangle}{\hat{H}|\psi\rangle} \\ -1 + \frac{\hbar}{2i}\frac{\left\{\ln(\hat{\rho}),\hat{H}\right\}_{\mathcal{B}}|\psi\rangle}{\langle\psi|\hat{H}} & 0 \end{bmatrix} \tag{30}$$

Equations (22) can be written in compact form as

$$\begin{aligned} \frac{\partial\boldsymbol{\zeta}}{\partial t} &= -\frac{i}{\hbar}\begin{bmatrix} \frac{\partial\mathcal{H}}{\partial|\psi\rangle} & \frac{\partial\mathcal{H}}{\partial\langle\psi|} \end{bmatrix}\cdot\boldsymbol{\Omega}\cdot\begin{bmatrix} \frac{\partial\boldsymbol{\zeta}}{\partial|\psi\rangle} \\ \frac{\partial\boldsymbol{\zeta}}{\partial\langle\psi|} \end{bmatrix} \\ &= -\frac{i}{\hbar}\{\mathcal{H},\boldsymbol{\zeta}\}_{\boldsymbol{\Omega};\zeta} \ . \end{aligned} \tag{31}$$

Equations (22), or their compact "Weinberg-like" form in Eq. (31), express the wave picture for the quantum-classical dynamics of phase space dependent quantum degrees of freedom [2, 3]. Such a wave picture makes one recognize the intrinsic non-linearity of quantum-classical dynamics. This specific features will be discussed, among other issues, in the next section.

IV. ADIABATIC BASIS REPRESENTATION AND SURFACE-HOPPING SCHEMES

Equations (22) are written in an abstract form. In order to devise a numerical algorithm to solve them one has to obtain a representation in some basis. Of course, any basis can be used but, since one would like to find a comparison with surface-hopping schemes, the adiabatic basis is a good choice. To this end, consider the following form of the quantum-classical Hamiltonian operator:

$$\hat{H} = \frac{P^2}{2M} + \hat{h}(R) \ , \tag{32}$$

where the first term provides the kinetic energy of the classical degrees of freedom with mass M while $\hat{h}(R)$ describes the quantum sub-system and its coupling with

the classical coordinates R. The adiabatic basis is then defined by the following eigenvalue equation:

$$\hat{h}|\alpha;R\rangle = E_\alpha(R)|\alpha;R\rangle \ . \tag{33}$$

Since the non-linear wave equations in (22) have been derived from the bracket equation for the quantum-classical density matrix (17), by dealing in a suitable manner with the Poisson bracket terms, the most simple way to find the representation of the wave equations (22) in the adiabatic basis is to first represent Eq. (17) in such a basis and then deal with the terms arising from the Poisson brackets. The adiabatic representation of Eq. (17) is [3]

$$\partial_t \rho_{\alpha\alpha'}(X,t) \ = \ -\sum_{\beta\beta'} i\mathcal{L}_{\alpha\alpha',\beta\beta'}\rho_{\beta\beta'}(X,t) \ , \tag{34}$$

where

$$\begin{aligned} i\mathcal{L}_{\alpha\alpha',\beta\beta'} \ &= \ i\mathcal{L}^{(0)}_{\alpha\alpha',\beta\beta'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'} \\ &= \ \left(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'}\right)\delta_{\alpha\beta}\delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'} \end{aligned} \tag{35}$$

Here, $\omega_{\alpha\alpha'} = \left(E_\alpha(R) - E_{\alpha'}(R)\right)/\hbar \equiv E_{\alpha\alpha'}/\hbar$ and

$$iL_{\alpha\alpha'} = \frac{P}{M}\cdot\frac{\partial}{\partial R} + \frac{1}{2}\left(F_\alpha + F_{\alpha'}\right)\frac{\partial}{\partial P} \ , \tag{36}$$

where

$$F_\alpha = -\langle\alpha;R|\frac{\partial\hat{h}(R)}{\partial R}|\alpha;R\rangle \tag{37}$$

is the Hellmann-Feynman force for state α. The operator J that describes nonadiabatic effects is

$$\begin{aligned} J_{\alpha\alpha',\beta\beta'} \ &= \ -\frac{P}{M}\cdot d_{\alpha\beta}\left(1+\frac{1}{2}S_{\alpha\beta}\cdot\frac{\partial}{\partial P}\right)\delta_{\alpha'\beta'} \\ &\quad -\frac{P}{M}\cdot d^*_{\alpha'\beta'}\left(1+\frac{1}{2}S^*_{\alpha'\beta'}\cdot\frac{\partial}{\partial P}\right)\delta_{\alpha\beta} \ , \end{aligned} \tag{38}$$

where $d_{\alpha\beta} = \langle\alpha;R|(\partial/\partial R)|\beta;R\rangle$ is the nonadiabatic coupling vector and

$$S_{\alpha\beta} = E_{\alpha\beta}d_{\alpha\beta}\left(\frac{P}{M}\cdot d_{\alpha\beta}\right)^{-1} \ . \tag{39}$$

Using Eqs. (36) and (38), the equation of motion for the density matrix in the adiabatic basis can be written explicitly as

$$\begin{aligned} \partial_t\rho_{\alpha\alpha'} \ &= \ -i\omega_{\alpha\alpha'}\rho_{\alpha\alpha'} - \frac{P}{M}\cdot\frac{\partial}{\partial R}\rho_{\alpha\alpha'} \\ &\quad -\frac{1}{2}\left(F_\alpha + F_{\alpha'}\right)\cdot\frac{\partial}{\partial P}\rho_{\alpha\alpha'} \\ &\quad -\sum_\beta \frac{P}{M}\cdot d_{\alpha\beta}\left(1+\frac{1}{2}S_{\alpha\beta}\cdot\frac{\partial}{\partial P}\right)\rho_{\beta\alpha'} \\ &\quad -\sum_{\beta'} \frac{P}{M}\cdot d^*_{\alpha'\beta'}\left(1+\frac{1}{2}S^*_{\alpha'\beta'}\cdot\frac{\partial}{\partial P}\right)\rho_{\alpha\beta'} \ . \end{aligned} \tag{40}$$

The wave fields $|\psi^\iota(X)\rangle$ and $\langle\psi^\iota(X)|$ can be expanded in the adiabatic basis as

$$\begin{aligned} |\psi^\iota(X)\rangle \ &= \ \sum_\alpha |\alpha;R\rangle\langle\alpha;R|\psi^\iota(X)\rangle = \sum_\alpha C^\iota_\alpha|\alpha;R\rangle \\ \langle\psi^\iota(X)| \ &= \ \sum_\alpha \langle\psi^\iota|\alpha;R\rangle\langle\alpha;R| = \sum_\alpha \langle\alpha;R|C^{\iota*}_\alpha(X) \ , \end{aligned} \tag{41}$$

and the density matrix in Eq. (20) becomes

$$\rho_{\alpha\alpha'}(X,t) \ = \ \sum_\iota w_\iota C^\iota_\alpha(X,t)C^{\iota*}_{\alpha'}(X,t) \ . \tag{42}$$

In order to find two separate equations for C^ι_α and $C^{\iota*}_{\alpha'}$, one cannot insert Eq. (42) directly into Eq. (40) because of the presence of the derivatives with respect to the phase space coordinates R ad P. One must set Eq. (40) into the form of a multiplicative operator acting on $\rho_{\alpha\alpha'}$. To this end, for example, consider

$$\begin{aligned} \frac{\partial}{\partial P}\rho_{\beta\alpha'} \ &= \ \sum_\gamma\left(\frac{\partial}{\partial P}\rho_{\beta\gamma}\right)\delta_{\gamma\alpha'} = \sum_{\gamma\mu}\left(\frac{\partial}{\partial P}\rho_{\beta\gamma}\right)\rho^{-1}_{\gamma\mu}\rho_{\mu\alpha'} \\ &= \ \sum_\mu \frac{\partial(\ln\hat{\rho})_{\beta\mu}}{\partial P}\rho_{\mu\alpha'} \ . \end{aligned} \tag{43}$$

Equation (43) shows how to transform formally a derivative operator acting on $\hat{\rho}$ into a multiplicative operator which, however, depends on $\hat{\rho}$ itself. Therefore, Eq. (40) becomes

$$\begin{aligned} \partial_t\rho_{\alpha\alpha'} \ &= \ -\frac{i}{\hbar}E_\alpha\rho_{\alpha\alpha'} + \frac{i}{\hbar}E_{\alpha'}\rho_{\alpha\alpha'} \\ &\quad - \ \sum_\beta \frac{P}{M}\cdot d_{\alpha\beta}\rho_{\beta\alpha'} - \sum_{\beta'}\frac{P}{M}\cdot d^*_{\alpha'\beta'}\rho_{\alpha\beta'} \\ &\quad - \ \frac{1}{2}\sum_\mu \frac{P}{M}\cdot\frac{\partial(\ln\rho)_{\alpha\mu}}{\partial R}\rho_{\mu\alpha'} \\ &\quad - \ \frac{1}{2}\sum_\mu \frac{P}{M}\cdot\frac{\partial(\ln\rho)_{\mu\alpha'}}{\partial R}\rho_{\alpha\mu} \\ &\quad - \ \frac{1}{2}\sum_\mu F_\alpha\frac{\partial(\ln\rho)_{\alpha\mu}}{\partial P}\rho_{\mu\alpha'} \\ &\quad - \ \frac{1}{2}\sum_\mu F_{\alpha'}\cdot\frac{\partial(\ln\rho)_{\mu\alpha'}}{\partial P}\rho_{\alpha\mu} \\ &\quad - \ \frac{1}{2}\sum_{\beta,\mu}\frac{P}{M}\cdot d_{\alpha\beta}S_{\alpha\beta}\cdot\frac{\partial(\ln\hat{\rho})_{\beta\mu}}{\partial P}\rho_{\mu\alpha'} \\ &\quad - \ \frac{1}{2}\sum_{\beta',\mu}\frac{P}{M}\cdot d^*_{\alpha'\beta'}S^*_{\alpha'\beta'}\cdot\frac{\partial(\ln\hat{\rho})_{\mu\beta'}}{\partial P}\rho_{\alpha\mu} \ . \end{aligned} \tag{44}$$

Inserting the adiabatic expression for the density matrix, given in Eq. (42), into Eq. (44), one obtains, for each quantum state ι, the following two coupled equations

$$\dot{C}^\iota_\alpha(X,t) \ = \ -\frac{i}{\hbar}E_\alpha C^\iota_\alpha(X,t) - \sum_\beta\frac{P}{M}\cdot d_{\alpha\beta}C^\iota_\beta(X,t)$$

$$
\begin{aligned}
&- \frac{1}{2}\sum_{\beta,\mu}\frac{P}{M}\cdot d_{\alpha\beta}S_{\alpha\beta}\cdot\frac{\partial(\ln\hat{\rho})_{\beta\mu}}{\partial P}C^{\iota}_{\mu}(X,t)\\
&- \frac{1}{2}\sum_{\mu}\frac{P}{M}\cdot\frac{\partial(\ln\rho)_{\alpha\mu}}{\partial R}C^{\iota}_{\mu}(X,t)\\
&- \frac{1}{2}\sum_{\mu}F_{\alpha}\frac{\partial(\ln\rho)_{\alpha\mu}}{\partial P}C^{\iota}_{\mu}(X,t) \qquad (45)
\end{aligned}
$$

$$
\begin{aligned}
\dot{C}^{\iota *}_{\alpha'}(X,t) &= +\frac{i}{\hbar}E_{\alpha'}C^{\iota *}_{\alpha'}(X,t)-\sum_{\beta'}\frac{P}{M}\cdot d^{*}_{\alpha'\beta'}C^{\iota *}_{\beta'}(X,t)\\
&- \frac{1}{2}\sum_{\beta',\mu}\frac{P}{M}\cdot d^{*}_{\alpha'\beta'}S^{*}_{\alpha'\beta'}\cdot\frac{\partial(\ln\hat{\rho})_{\mu\beta'}}{\partial P}C^{\iota *}_{\mu}(X,t)\\
&- \frac{1}{2}\sum_{\mu}\frac{P}{M}\cdot\frac{\partial(\ln\rho)_{\mu\alpha'}}{\partial R}C^{\iota *}_{\mu}(X,t)\\
&- \frac{1}{2}\sum_{\mu}F_{\alpha'}\cdot\frac{\partial(\ln\rho)_{\mu\alpha'}}{\partial P}C^{\iota *}_{\mu}(X,t)\ . \qquad (46)
\end{aligned}
$$

Quantum-classical averages of arbitrary observables can be calculated in the adiabatic as

$$
\langle\hat{\chi}\rangle(t)=\sum_{\iota}w_{\iota}\sum_{\alpha\alpha'}\int dX C^{\iota}_{\alpha}(X,t)C^{\iota *}_{\alpha'}(X,t)\chi_{\alpha'\alpha}(X)\ , \qquad (47)
$$

where the coefficients $C^{\iota}_{\alpha}(X,t)$ and $C^{\iota *}_{\alpha'}(X,t)$ are evolved according to Eqs. (45) and (46), respectively. Equations (45) and (46) are non-linear equations which couple all the adiabatic states used to analyze the system.

At this stage, a general discussion about such a non-linear character is required. With a wide consensus, quantum mechanics is considered a linear theory. This leads, for example, to the visualization of quantum transitions as instantaneous *quantum jumps*. The linearity of the theory also determines the need of considering infinite perturbative series which must be re-summed in some way in order to extract meaningful predictions. Density Functional Theory is an example of a non-linear theory [18] but it is usually considered just as a computational tool. However, there are other approaches to quantum classical theory that represent interactions by an intrinsic non-linear scheme [19]. It is not difficult to see how this is possible. Matter is represented by waves, these very same waves enter into the definition of the fields defining their interaction [20]. This point of view has been pursued by Jaynes [21] and Barut [22], among others. These non-linear approaches depict quantum transitions as abrupt but continuous events [19] in which, to go from state $|1\rangle$ to state $|2\rangle$, the system is first brought by the interaction in a superposition $\alpha|1\rangle+\beta|2\rangle$, and then, as the interaction ends, it finally goes to state $|2\rangle$. It is understood that this is made possible by the non-linearity of such theories because, instead, a linear theory would preserve the superposition indefinitely. Incidentally, the picture of the transition process just depicted also emerges from the numerical implementation [5] of the nonadiabatic quantum-classical dynamics of phase space dependent operators [2, 3]: The action of the operator J in Eq. (35) can build and destroy coherence in the system by creating and destroying superposition of states. As explained above, this is a feature of a non-linear theory. Such a non-linear character is simply hidden in the operator version of quantum-classical dynamics and clearly manifested by the wave picture of the quantum-classical evolution, which has been introduced in this paper.

Since Eqs. (45) and (46) are non-linear, their numerical integration requires either to adopt an iterative self-consistent procedure (according to which one makes a first guess of $\rho_{\alpha\alpha'}$, as dictated by Eq. (42), calculates the evolved $C^{\iota}_{\alpha}(X,t)$ and $C^{\iota *}_{\alpha'}(X,t)$, and then goes into a recursive procedure until numerical convergence is obtained) or to choose a definite form for $\rho^{G}_{\alpha\alpha'}$, following physical intuition, and then calculating the time evolution, according to the form of Eqs. (45) and (46) which is obtained by using $\rho^{G}_{\alpha\alpha'}$. This last method is already known within the Wigner formulation of quantum mechanics [23] as the method of *Wigner trajectories* [24]. It is also important to find some importance sampling scheme for the phase space integral in Eq. (47). Such sampling scheme may depend on the specific form $\chi_{\alpha\alpha'}$ of the observable. It is interesting to note that Eqs. (45), (46), and (47) can be used to address both equilibrium and non-equilibrium problems on the same footing. However, the dynamical picture provided by Eqs. (45) and (46) is very different both from that of the usual surface-hopping schemes [25] and from that of the nonadiabatic evolution of quantum-classical operators [5]. In order to appreciate this, for simplicity, one can consider a situation in which there is no thermal disorder in the quantum degrees of freedom so that $\iota = 1$: *viz.*, the density matrix becomes that of a pure state $\rho_{\alpha\alpha'}(X,t) \rightarrow C_{\alpha}(X,t)C^{*}_{\alpha'}(X,t)$. Then, equations (45) and (46) remain unaltered and one has just to remove the index ι from the coefficients. Therefore, it can be realized that no classical trajectory propagation, and no state switching are involved by Eqs. (45) and (46). Instead, in order to calculate averages according to Eq. (47), one has to sample phase space points and integrate the matrix equations.

In the next section, an equilibrium approximation of Eqs. (45) and (46), along the lines followed by the method of *Wigner trajectories* [24], is given and applied, with good numerical results, to the adiabatic and nonadiabatic dynamics of the spin-boson model.

V. WAVE DYNAMICS OF THE SPIN-BOSON MODEL

The theory developed in the previous sections can be applied to simulate the relaxation dynamics of the spin-boson system [26]. This system has already been studied within the framework of quantum-classical dynamics of operators in Refs. [9]. Using the dimensionless variables of Refs. [9], the quantum-classical Hamiltonian operator

of the spin-boson system reads

$$\begin{aligned}\hat{H}(X) &= -\Omega\hat{\sigma}_x + \sum_{j=1}^{N}\left(\frac{P_j^2}{2} + \frac{1}{2}\omega_j^2 R_j^2 - c_j\hat{\sigma}_z R_j\right) \\ &= \hat{h}_s + H_b + \hat{V}_c(R) \,, \end{aligned} \tag{48}$$

where $\hat{h}_s = -\Omega\hat{\sigma}_x$ is the subsystem Hamiltonian, $H_b = \sum_{j=1}^{N} P_j^2/2 + 1/2\omega_j^2 R_j^2 = \sum_{j=1}^{N} P_j^2/2 + V_b(R)$ is the Hamiltonian of a classical bath of N harmonic oscillators, and $\hat{V}_c(R) = -\sum_{j=1}^{N} c_j\hat{\sigma}_z R_j = \gamma(R)\hat{\sigma}_z$ is the interaction between the subsystem and the bath. An Ohmic spectral density is assumed for the bath. Hence, denoting the Kondo parameter as ξ_K and the cut-off frequency as $\omega_{\max}$, the frequencies of the oscillators are defined by $\omega_j = -\ln(1 - j\omega_0)$, where $\omega_0 = N^{-1}(1 - \exp(-\omega_{\max}))$, and the constants entering the coupling by and $c_j = \sqrt{\xi_K\omega_0}\ \omega_j$. The adiabatic eigenvalues and eigenvectors, respectively, are

$$E_{1,2} = V_b \mp \sqrt{\Omega^2 + \gamma^2(R)} \,, \tag{49}$$

$$\begin{aligned}|1;R\rangle &= \frac{1}{\sqrt{2(1+G^2}}\begin{pmatrix} 1+G \\ 1-G \end{pmatrix} \\ |2;R\rangle &= \frac{1}{\sqrt{2(1+G^2}}\begin{pmatrix} -1+G \\ 1+G \end{pmatrix} \,, \end{aligned} \tag{50}$$

where

$$G(R) = \gamma^{-1}(R)\left[-\Omega + \sqrt{\Omega^2 + \gamma^2(R)}\right] \,. \tag{51}$$

The coupling vector $d_{\alpha\alpha'} = \langle\alpha;R|\overrightarrow{\partial}/\partial R|\alpha';R\rangle$ is

$$d_{12} = -d_{21} = (1+G^2)^{-1}\partial G/\partial R \,. \tag{52}$$

Assuming an initially uncorrelated density matrix, where the bath is in thermal equilibrium and the subsystem is in state $|\uparrow\rangle$, the initial quantum-classical density matrix in the adiabatic basis takes the form

$$\boldsymbol{\rho}(0) = \boldsymbol{\rho}_s(0)\rho_b(X) \,, \tag{53}$$

where

$$\boldsymbol{\rho}_s(0) = \frac{1}{2(1+G^2)}\begin{pmatrix} (1+G)^2 & 1-G^2 \\ 1-G^2 & (1-G)^2 \end{pmatrix} \,, \tag{54}$$

and

$$\begin{aligned}\rho_b(X) &= \prod_{I=1}^{N}\frac{\tanh(\beta\omega_i/2)}{\omega_i} \\ &\times \exp\left[-\frac{2\tanh(\beta\omega_i/2)}{\omega_i}\left(\frac{P_i^2}{2} + \frac{\omega_i^2 R_i^2}{2}\right)\right] \,. \end{aligned} \tag{55}$$

The process of relaxation from the initial state can be followed by monitoring the subsystem observables $\hat{\sigma_z}$, which in the adiabatic basis reads

$$\boldsymbol{\sigma}_z = \frac{1}{1+G^2}\begin{pmatrix} 2G & 1-G^2 \\ 1-G^2 & -2G \end{pmatrix} \,. \tag{56}$$

The adiabatic basis is real so that the initial density matrix of the system can be written as

$$\rho_{\alpha\alpha'}(X,0) = \sum_{\alpha=1}^{2}\psi_\alpha(X,0)\phi_{\alpha'}(X,0) \,, \tag{57}$$

where

$$\psi_1(X,0) = \phi_1(X,0) = \sqrt{\rho_b(X)}\frac{1+G}{\sqrt{2(1+G^2)}} \,, \tag{58}$$

$$\psi_2(X,0) = \phi_2(X,0) = \sqrt{\rho_b(X)}\frac{1-G}{\sqrt{2(1+G^2)}} \,. \tag{59}$$

Such coefficients enter into the calculation of the observable

$$\langle\boldsymbol{\sigma}_z(t)\rangle = \sum_{\alpha\alpha'}\int dX\phi_{\alpha'}(X,t)\sigma_z^{\alpha'\alpha}(X)\psi_\alpha(X,t) \,. \tag{60}$$

The coefficients evolve in time according to Eqs. (45) and (46), where one must set $C_\alpha^\iota \equiv \psi_\alpha$ and $C_{\alpha'}^{\iota *} \equiv \phi_{\alpha'}$. In order to devise an effective computational scheme for such equations, one could assume that the density matrix entering Eqs. (45) and (46) is taken to be that at $t = \infty$, when the total system (subsystem plus bath) has reached thermal equilibrium. The equilibrium quantum-classical density matrix is known as a series expansion in $\hbar$ [4]. If one makes the additional assumption of complete decoherence at $t = \infty$, only the $\mathcal{O}(\hbar^0)$ term can be taken

$$\rho_e^{(0)\alpha\alpha'}(X) = Z_0^{-1}e^{-\beta(\sum_j P_j^2/2 + E_\alpha(R))}\delta_{\alpha\alpha'} \,, \tag{61}$$

where $Z_0 = \sum_{\alpha\alpha'}\int dX\rho_e^{(0)\alpha\alpha'}(X)$. Then

$$\frac{\partial\ln\rho_e^{(0)\alpha\alpha'}}{\partial R} = -\beta\frac{\partial E_\alpha}{\partial R}\delta_{\alpha\alpha'} \equiv \beta F_\alpha(R)\delta_{\alpha\alpha'} \,, \tag{62}$$

$$\frac{\partial\ln\rho_e^{(0)\alpha\alpha'}}{\partial P} = -\beta P\delta_{\alpha\alpha'} \,. \tag{63}$$

Equations (45) and (46) become

$$\begin{aligned}\frac{d}{dt}\psi_\alpha(X,t) &= -iE_\alpha\psi_\alpha(X,t) \\ &- \sum_\beta P\cdot d_{\alpha\beta}\left(1 - \frac{\beta}{2}E_{\alpha\beta}\right)\psi_\beta(X,t) \end{aligned} \tag{64}$$

$$\begin{aligned}\frac{d}{dt}\phi_{\alpha'}(X,t) &= iE_{\alpha'}\phi_{\alpha'}(X,t) \\ &- \sum_{\beta'} P\cdot d_{\alpha'\beta'}\left(1 - \frac{\beta}{2}E_{\alpha'\beta'}\right)\phi_{\beta'}(X,t) \,. \end{aligned} \tag{65}$$

In Eqs. (46) and (65) the terms $\pm(\beta/2)P\cdot F_\alpha\psi_\alpha$ (and the analogous terms with $\xi_{\alpha'}$) cancel each other. In the

adiabatic basis $d_{11}(R) = d_{22}(R) = 0$. Hence, defining the matrix

$$\mathbf{\Sigma} = \begin{bmatrix} -iE_1 & -P \cdot d_{12} \left(1 - \frac{\beta}{2} E_{12}\right) \\ P \cdot d_{12} \left(1 + \frac{\beta}{2} E_{12}\right) & -iE_2 \end{bmatrix} , \tag{66}$$

Equations (64) and (65) can be written as

$$\frac{d}{dt} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \mathbf{\Sigma} \cdot \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} , \quad \frac{d}{dt} \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} = \mathbf{\Sigma}^* \cdot \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} , \tag{67}$$

which can be integrated by means of the simple algorithm $\mathbf{\Psi}(X, d\tau) = \mathbf{\Psi}(X, 0) + d\tau \mathbf{\Theta}(X, 0) \cdot \boldsymbol{\eta}(X, 0)$, where $\mathbf{\Psi} = (\boldsymbol{\psi}, \boldsymbol{\phi})$ and $\mathbf{\Theta} = (\mathbf{\Sigma}, \mathbf{\Sigma}^*)$. The phase space part of the initial values of $\boldsymbol{\psi}$ and $\boldsymbol{\phi}$ can be used as the weight for sampling the coordinates X entering the classical integral in Eq. (60). Then, for each initial value X, Eqs. (67) must be integrated in time so that averages can be calculated. It is worth to note that in such a wave scheme the Eulerian point of view of quantum-classical dynamics [5, 9] is preserved. This is different from what happens in the original operator approach [5, 9], where in order to devise an effective time integration scheme by means of the Dyson expansion, one is forced to change from the Eulerian point of view (according to which the phase space point is fixed and the quantum degrees of freedom evolve in time *at* this fixed phase space point) to the Lagrangian point of view, where phase space trajectories are generated. Moreover, it must be noted that the numerical integration of Eqs. (67) provides directly the nonadiabatic dynamics without the need to introduce surface-hopping approximations.

In order to be able of comparing the results with those presented in Refs. [9], the numerical values of the parameters specifying the spin-boson system have been chosen to be $\beta = 0.3$, $\Omega = 1/3$, $\omega_{\max} = 3$, $\xi_K = 0.007$, and $N = 200$. Figure 1 shows the results obtained in the adiabatic case, obtained by setting $d_{12} = 0$ in Eqs. (67). One can see that, in spite of the simple approximation of assuming the equilibrium density matrix in the equations of motion, the wave theory provides results which are in good agreement with those obtained with the more sophisticated operator approach of Refs. [9]. Instead, Fig. 2 shows the results of the nonadiabatic calculation. This is to be compared with the results of the operator theory [9]. Of course, since different ways of dealing with the nonadiabatic effects are used in the two approaches the results do not need to be the same. However, the results of the wave theory follow qualitatively those of Refs. [9] while improving substantially the statistical convergence and increasing the length of the time interval spanned by a factor of $2 - 3$. Such results are particularly encorauging and suggest the possible application of the wave theory here proposed, for example, to the calculation of nonadiabatic rate constants of complex systems in the condensed phase [1].

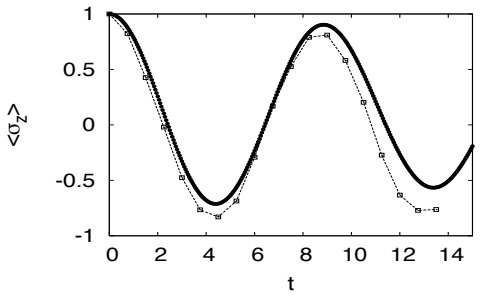

FIG. 1: Adiabatic dynamics of the spin-boson model. $\beta = 0.3$, $\Omega = 1/3$, $\omega_{\max} = 3$, $\xi_K = 0.007$, $N = 200$. The black circles show the results of the calculation with the theory proposed in this paper while the light dashed line with squares shows, for comparison, the results of the calculation in Refs. [9].

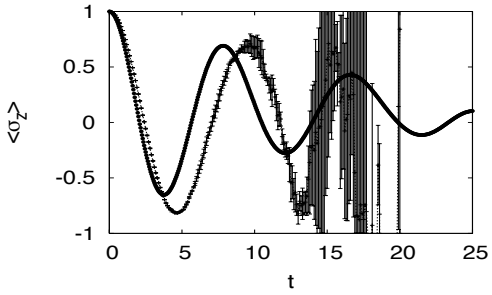

FIG. 2: Nonadiabatic dynamics of the spin-boson model. $\beta = 0.3$, $\Omega = 1/3$, $\omega_{\max} = 3$, $\xi_K = 0.007$, $N = 200$. The black circles show the results of the calculation with the theory proposed in this paper while the line with error bars shows, for comparison, the results of the calculation in Refs. [9].

VI. CONCLUSIONS

In this paper the approach to the quantum-classical mechanics of phase space dependent operators has been remodeled as a non-linear formalism for wave fields. It has been shown that two coupled non-linear equations for phase space dependent wave fields correspond to the single equation for the quantum-classical density matrix in the operator scheme of motion. The equations of motion for the wave fields have been re-expressed by means of a suitable bracket and it has been shown that the emerging formalism generalizes within a non-Hamiltonian framework the non-linear quantum mechanical formalism that has been proposed recently by Weinberg. Finally, the non-linear wave equations have been represented into the adiabatic basis and have been applied, after a suitable equilibrium approximation, to the numerical study of the adiabatic and nonadiabatic dynamics of the spin-boson model. Good results have been obtained. In particular, the time interval that can be spanned by the nonadiabatic calculation within the wave scheme of motion turns out to be a factor of two-three longer than that accessible within the operator scheme of motion. This encourages one to pursue the application of the wave scheme of mo-

tion to the calculation of correlation functions for systems in the condensed phase. Future works will be specifically devoted to such an issue.

Acknowledgment
I acknowledge Professor Kapral for suggesting the possibility of mapping the quantum-classical dynamics of operators into a wave scheme of motion. I am also very grateful to Professor P. V. Giaquinta for continuous encouragement and suggestions.

APPENDIX A: WEINBERG'S FORMALISM

Consider a quantum system in a state described by the wave fields $|\Psi\rangle$ and $\langle\Psi|$, where Dirac's bra-ket notation is used to denote $\Psi(r) \equiv \langle r|\Psi\rangle$ and $\Psi^*(r) \equiv \langle\Psi|r\rangle$. Observables are defined by functions of the type

$$a = \langle\Psi|\hat{A}|\Psi\rangle \ , \tag{A1}$$

where the operators are Hermitian, $\hat{A} = \hat{A}^\dagger$. Weinberg's formalism can be introduced by defining Poisson brackets in terms of the wave fields $|\Psi\rangle$ and $\langle\Psi|$. To this end, one considers the wave fields as "phase space" coordinates $\boldsymbol{\zeta} \equiv (|\Psi\rangle, \langle\Psi|)$, so that $\zeta_1 = |\Psi\rangle$ and $\zeta_2 = \langle\Psi|$, and then introduce brackets of observables as

$$\{a, b\}_{\boldsymbol{\mathcal{B}}} \ = \ \sum_{\alpha=1}^{2} \frac{\partial a}{\partial \zeta_\alpha} \mathcal{B}_{\alpha\beta} \frac{\partial b}{\partial \zeta_\beta} \ . \tag{A2}$$

The bracket in Eq. (A2) defines a Lie algebra and a Hamiltonian systems. Typically, the Jacobi relation is satisfied, *i.e.* $\mathcal{J} = \{a, \{b, c\}_{\boldsymbol{\mathcal{B}}}\}_{\boldsymbol{\mathcal{B}}} + \{c\,\{a, b\}_{\boldsymbol{\mathcal{B}}}\}_{\boldsymbol{\mathcal{B}}} + \{b, \{c, a\}_{\boldsymbol{\mathcal{B}}}\}_{\boldsymbol{\mathcal{B}}} = 0$. In order to obtain the usual quantum formalism, one can introduce the Hamiltonian functional in the form

$$\mathcal{H}[|\psi\rangle, \langle\psi|] \equiv \mathcal{H}[\boldsymbol{\zeta}] = \langle\psi|\hat{H}|\psi\rangle \ , \tag{A3}$$

where $\hat{H}$ is the Hamiltonian operator of the system. Equations of motion for the wave fields can be written in compact form as

$$\frac{\partial \boldsymbol{\zeta}}{\partial t} = \frac{i}{\hbar} \{\mathcal{H}[\boldsymbol{\zeta}], \boldsymbol{\zeta}\}_{\boldsymbol{\mathcal{B}}} \ . \tag{A4}$$

The compact form of Eq. (A4) can be set into an explicit form as

$$\frac{\partial}{\partial t}|\Psi\rangle \ = \ \frac{i}{\hbar} \frac{\partial \mathcal{H}}{\partial \langle\Psi|} \mathcal{B}_{21} \tag{A5}$$

$$\frac{\partial}{\partial t}\langle\Psi| \ = \ \frac{i}{\hbar} \frac{\partial \mathcal{H}}{\partial |\Psi\rangle} \mathcal{B}_{12} \ . \tag{A6}$$

It is easy to see that, when the Hamiltonian function is chosen as in Eq. (A3), Eqs. (A4), or their explicit form (A5-A6), gives the usual formalism of quantum mechanics. It is worth to remark that in order not to alter gauge invariance, the Hamiltonian and the other observables must obey the homogeneity condition

$$\mathcal{H} = \langle\Psi|(\partial\mathcal{H}/\partial\zeta_2)\rangle = \langle(\partial\mathcal{H}/\partial\zeta_1)|\Psi\rangle \ . \tag{A7}$$

Weinberg showed how the formalism above given can be generalized in order to describe non-linear effects in quantum mechanics [11]. To this end, one must maintain the homogeneity condition, Eq. (A7), on the Hamiltonian but relax the constraint which assumes that the Hamiltonian must be a bilinear function of the wave fields. Thus, the Hamiltonian can be a general function given by

$$\tilde{\mathcal{H}} = \sum_{i=1}^{n} \rho^{-i} \mathcal{H}_i \ , \tag{A8}$$

where n is arbitrary integer that fixes the order of the correction, $\mathcal{H}_0 = h$, and

$$\begin{aligned} \mathcal{H}_1 \ &= \ \rho^{-1} \int dr dr' dr'' dr''' \Psi^*(r)\Psi^*(r') \\ &\times \ G(r, r', r'', r''')\Psi(r'')\Psi(r''') \ , \end{aligned} \tag{A9}$$

with analogous expressions for higher order terms. Applications and thorough discussions of the above formalism can be found in Ref. [11].

Once Weinberg's formalism is expressed by means of the symplectic form in Eq. (A4), it can be generalized very easily in order to obtain a non-Hamiltonian quantum algebra. To this end, one can substitute the antisymmetric matrix $\boldsymbol{\mathcal{B}}$ with another antisymmetric matrix $\boldsymbol{\Omega} = \boldsymbol{\Omega}[\boldsymbol{\zeta}]$, whose elements might be functionals of $\boldsymbol{\zeta} \equiv (|\Psi\rangle, \langle\Psi|)$ obeying the homogeneity condition in Eq. (A7). By means of $\boldsymbol{\Omega}$ a non-Hamiltonian bracket $\{\ldots, \ldots\}_{\boldsymbol{\Omega}}$ can be defined as

$$\{a, b\}_{\boldsymbol{\Omega}} \ = \ \sum_{\alpha=1}^{2} \frac{\partial a}{\partial \zeta_\alpha} \Omega_{\alpha\beta}[\zeta] \frac{\partial b}{\partial \zeta_\beta} \ . \tag{A10}$$

In general, the bracket in Eq. (A10) does no longer satisfy the Jacobi relation

$$\mathcal{J} = \{a, \{b, c\}_{\boldsymbol{\Omega}}\}_{\boldsymbol{\Omega}} + \{c\,\{a, b\}_{\boldsymbol{\Omega}}\}_{\boldsymbol{\Omega}} + \{b, \{c, a\}_{\boldsymbol{\Omega}}\}_{\boldsymbol{\Omega}} \neq 0 \ . \tag{A11}$$

Thus, non-Hamiltonian equations of motion can be written as

$$\frac{\partial \boldsymbol{\zeta}}{\partial t} = \frac{i}{\hbar} \{\mathcal{H}, \boldsymbol{\zeta}\}_{\boldsymbol{\Omega}} \ . \tag{A12}$$

In principle, the non-Hamiltonian theory, specified by Eqs. (A10), (A11), and (A12), can be used to address the problem of non-linear correction to quantum mechanics, as it was done in Refs. [11]. In the present paper, it has been shown that such a non-Hamiltonian and non-linear version of quantum mechanics is already implied when one formulates quantum-classical dynamics of operators by means of suitable brackets. As a matter of fact, it was shown that the quantum-classical theories of Refs. [2, 3] can be mapped onto a wave formalism which has precisely the same form specified by Eqs. (A10), (A11), and (A12).

[1] R. Kapral and A. Sergi, in *Handbook of Theoretical and Computational Nanotechnology*, Vol. 1 Ch. 92, eds. M. Rieth and W. Schommers (American Scientific Publishers, 2005).

[2] I. V. Aleksandrov, Z. Naturforsch., **36a**, 902 (1981); V. I. Gerasimenko, Theor. Math. Phys., **50**, 77 (1982); D. Ya. Petrina, V. I. Gerasimenko and V. Z. Enolskii, Sov. Phys. Dokl., **35**, 925 (1990); W. Boucher and J. Traschen, Phys. Rev. D, **37**, 3522 (1988); W. Y. Zhang and R. Balescu, J. Plasma Phys., **40**, 199 (1988); R. Balescu and W. Y. Zhang, J. Plasma Phys. **40**, 215 (1988); O. V. Prezhdo and V.V. Kisil, Phys. Rev. A, **56**, 162 (1997); C. C. Martens and J.-Y. Fang, J. Chem. Phys. **106**, 4918 (1996); A. Donoso and C. C. Martens, J. Phys. Chem. **102**, 4291 (1998).

[3] R. Kapral and G. Ciccotti, J. Chem. Phys., **110**, 8919 (1999).

[4] S. Nielsen, R. Kapral, and G. Ciccotti J. Chem. Phys. **115** 5805 (2001).

[5] A. Sergi and R. Kapral, J. Chem. Phys. **118**, 8566 (2003); A. Sergi and R. Kapral, J. Chem. Phys. **119**, 12776 (2003); A. Sergi and R. Kapral, Comp. Phys. Comm. **169**, 400 (2005); A. Sergi and R. Kapral, J. Chem. Phys. **123**, 029902(2005); G. Hanna and R. Kapral, J. Chem. Phys. **122** 244505 (2005);

[6] A. Sergi, Phys. Rev. E **72**, 066125 (2005).

[7] A. Sergi, J. Chem. Phys. **124**, 024110 (2006).

[8] L. E. Ballentine, Quantum Mechanics. A Modern Development (World Scientific, Singapore, 2001).

[9] A. Sergi, D. Mac Kernan, G. Ciccotti, and R. Kapral, Theor. Chem. Acc. **110** 49 (2003); D. Mac Kernan, G. Ciccotti, and R. Kapral, J. Phys. Condens. Matt. **14** 9069 (2002); D. Mac Kernan, G. Ciccotti, and R. Kapral, J. Chem. Phys. **116** 2346 (2002).

[10] F. Strocchi, Rev. Mod. Phys. **38** 36 (1996); Y. Nambu, Phys. Rev. D **7** 2405 (1973); F. B. Eastbrook, Phys. Rev. D **8** 8 (1973); F. Bayen and M. Flato, Phys. Rev. D **10** 3049 (1975); A. Heslot, Phys. Rev. D **31** 1341 (1985); K. R. W. Jones, Phys. Rev. D **45** R2590 (1992), Phys. Rev. A **48** 822 (1993), Phys. Rev. A **50** 1062 (1994).

[11] S. Weinberg, Phys. Rev. Lett. **62** 485 (1989); Ann. Phys. **194** 336 (1989).

[12] I. Bialynicki-Birula and J. Mycielski, Ann. Phys. **100** 62 (1976); A. Shimony, Phys. Rev. A **20** 394 (1979); C. G. Shull, D. K. Atwood, J. Arthur, and M. A. Horne, Phys. Rev. Lett. **44** 765 (1980); R. Gähler, A. G. Klein, and A. Zeilinger, Phys. Rev. **23** 1611 (1981); R. Haag and U. Banner, Commun. Math. Phys. **60** 1 (1978); T. Kibble, Commun. Math. Phys. **64** 73 (1978).

[13] H. Goldstein, *Classical Mechanics* (Addison-Wesley, London, 1980); J. L. McCauley, *Classical Mechanics* (Cambridge University Press, Cambridge, 1997).

[14] A. Sergi and M. Ferrario, Phys. Rev. E **64** 056125 (2001); A. Sergi, Phys. Rev. E **67** 021101 (2003), Phys. Rev. E **69** 021109 (2004), Phys. Rev. E **72** 031104 (2005), Atti Accad. Pelorit. Pericol. Cl. Sci. Fis. Mat. Nat. **33** c1a0501003 (2005).

[15] I. Horenko, M. Weiser, B. Schmidt, and C. Schütte, J. Chem. Phys. **120** 8913 (2004); I. Horenko, B. Schmidt, and C. Schütte, J. Chem. Phys. **117** 4643 (2002); I. Horenko, C. Salzmann, B. Schmidt, and C. Schütte, J. Chem. Phys. **117** 11075 (2002); I. Horenko, B. Schmidt, and C. Schütte, J. Chem. Phys. **115** 5733 (2001); C. C. Wan and J. Schofield, J. Chem. Phys. **116** 494 (2002); J. Chem. Phys. **113** 7047 (2000); J. Chem. Phys. **112** 4447 (2000).

[16] R. Balescu, *Equilibrium and non equilibrium statistical mechanics*, (Wiley, New York 1975).

[17] Following another route, these equations were first derived by R. Kapral in a set of unpublished notes.

[18] W. Kohn, Rev. Mod. Phys. **71** 1253 (1999); R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer-Verlag, Berlin, 1991).

[19] C. A. Mead, *Collective Electrodynamics. Quantum Foundations of Electromagnetism* (MIT press, Cambridge-Massachussetts, 2002).

[20] S.-I. Tomonaga, *Quantum Mechanics* Vol. II (North-Holland, Amsterdam, 1961).

[21] E. T. Jaynes, *Microwave Laboratory Report No. 502* (Standford University, Standford, 1958); E. T. Jaynes and F. W. Cunnings, *Proceedings of the IEEE* p. 89 (1963); M. D. Crisp and E. T. Jaynes, Phys. Rev. **179**, 1253 (1969); **185**, 2046 (E) (1969), C. R. Stroud and Jaynes, Phys. Rev. A **1**, 106 (1970); Phys. Rev. A **2**, 260 (1970).

[22] A. O. Barut, J. Kraus, Y. Salamin, and N. Ünal, Phys. Rev. A. **45**, 7740 (1992); A. O. Barut and J. P. Dowling, Phys. Rev. A **43** 4060 (1991); Phys. Rev. A **41**, 2284 (1990); Phys. Rev. A **41**, 2277 (1990); Phys. Rev. A **36**, 649 (1987); A. O. Barut, Phys. Rev. A **34** 3502 (1986).

[23] H.-W. Lee, Phys. Rep. **259**, 147 (1995).

[24] H.-W. Lee and M. O. Scully, J. Chem. Phys. **77** 4604 (1982); H.-W. Lee, Phys. Lett. A **146**, 287 (1990), Found. Phys. **22**, 995 (1992).

[25] J. C. Tully and R. K. Preston, J. Chem. Phys. **55**, 562 (1971); J. R. Stine and J. T. Muckerman, J. Chem. Phys. **65**, 3975 (1976); N. C. Blais and D. G. Truhlar, J. Chem. Phys. **79**, 1334 (1983); G. Parlant and E. A. Gislason, J. Chem. Phys. **91**, 4416 (1989); J. C. Tully, J. Chem. Phys. **93**, 1061 (1990); A. J. Marks and D. L. Thompson, J. Chem. Phys. **95**, 8056 (1991); P. J. Kuntz, J. Chem. Phys. **95**, 141 (1991); F. J. Webster, P. J. Rossky and R. A. Friesner, Comput. Phys. Commun. **63**, 494 (1991); F. J. Webster, J. Schnitker, M. S. Friedrichs, R. A. Friesner, and P. J. Rossky, Phys. Rev. Lett. **66**, 3172 (1991); S. Chapman, Adv. Chem. Phys. **82**, 423 (1992); I. H. Gersonde and H. Gabriel, J. Chem. Phys. **98**, 2094 (1993); D. F. Coker, in *Computer Simulation in Chemical Physics*, p. 315 eds. M. P. Allen and D. J. Tildsley (Kluwer Academy, Dordecht, 1993); S. Hammes-Schiffer and J. C. Tully, J. Chem. Phys. **101**, 4657 (1994); B. R. Smith, M. J. Bearpark, M. A. Robb, F. Bernardi, and M. Olivucci, Chem. Phys. Lett. **242**, 27 (1995); V. D. Vachev, J. H. Frederick, B. A. Grishanin, V. A. Zadkov, and N. I. Koroteev, J. Phys. Chem. **99**, 5247 (1995); D. F. Coker and L. Xiao, J. Chem. Phys. **102**, 496 (1995); K. R. W. Jones, Phys. Rev. Lett. **76**, 4087 (1996); H. S. Mei and D. F. Coker, J. Chem. Phys. **104**, 4755 (1996); A. Ferretti, G. Granucci, A. Lami, M. Persico, and G. Villani, J. Chem. Phys. **104**, 5517 (1996); A. I. Krylov, R. B. Gerber, and R. D. Coalson, J. Chem. Phys. **105**,

4626 (1996); M. Ito and I. Ohmine, J. Chem. Phys. **106**, 3159 (1997); U. Muller and G. Stock, J. Chem. Phys. **107**, 6230 (1997). J. F. Yang and S. Hammes-Schiffer, J. Chem. Phys. **106**, 8442 (1997); J. Morelli and S. Hammes-Schiffer, Chem. Phys. Lett. **269**, 8442 (1997); O. V. Prezhdo and P. J. Rossky, J. Chem. Phys. **107**, 825 (1997); J. Y. Fang and S. Hammes-Schiffer, J. Chem. Phys. **110**, 11166 (1999); D. C. Borgis, S. Y. Lee, and J. T. Hynes, Chem. Phys. Lett. **162**, 19 (1989); D. C. Borgis and J. T. Hynes, J. Chem. Phys. **94**, 3619 (1991); H. Azzouz and D. C. Borgis, *ibid.* **98**, 7361 (1993); L. Xiao and D. F. Coker, J. Chem. Phys. **102**, 496 (1995); V. S. Batista and D. F. Coker, *ibid.* **110**, 6583 (1999); O. V. Prezhdo and P. J. Rossky, J. Chem. Phys. **107**, 5863 (1997); R. E. Cline and P. G. Wolynes, J. Chem. Phys. **86**, 3836 (1987); J. C. Tully, in *Classical and Quantum Dynamics in the Condensed Phase*, p. 489 (World Scientific, Singapore, 1998); S. Y. Kim and S. Hammes-Schiffer J. Chem. Phys. **124**, 244102 (2006).

[26] A. J. Legget, S. Chakravarty, A. T. Dorsey, M. P. A. Fischer, A. Garg, and M. Zwerger, Rev. Mod. Phys. **59** 1 (1987).